

the a values for m -fluorines are weaker and negative.⁹ Such a pattern is quite different from the one we derive for the pentafluorophenyl radical, implying that this radical does not have appreciable π character.

The theoretical understanding of fluorine hyperfine interactions appears to be less than adequate.¹⁰ Nevertheless, we explain the large positive coupling of ortho substituents by a direct interaction with the half-filled σ orbital at C-1. For the meta and para positions the contributions of direct coupling will be smaller and the a values of these nuclei will depend on a variety of factors including the polarization of the C-F bond and the s electrons of the fluorine atoms due to the unpaired spin on carbon and on fluorine. Since it is conceivable that these contributions are sensitive to the nature of substituents, the observed difference in the sign of $a_{\text{F}^{\text{p}}}$ for the p -fluorophenyl and the pentafluorophenyl radical does not appear internally inconsistent.

We conclude with a comment on the benzoyloxy radicals which we and others have assumed as intermediates. We have observed weak CIDNP signals for the o -fluorine nuclei of the benzoyloxy segments of **2** and of o -fluorophenyl o -fluorobenzoate. These signals indicate that the hyperfine coupling constants ($a_{\text{F}^{\text{o}}}$) of o -fluoro- and pentafluorobenzoyloxy radicals are positive. This limited information falls far short of elucidating the nature of fluorine-substituted benzoyloxy radicals.¹¹

(9) (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962); (b) A. Carrington, A. Hudson, and H. C. Longuet-Higgins, *ibid.*, **9**, 377 (1965); (c) A. Hinchcliffe and J. N. Murrell, *ibid.*, **14**, 147 (1968); (d) W. G. Espersen and R. W. Kreilick, *ibid.*, **16**, 577 (1969); (e) J. W. Rakshys, *Chem. Commun.*, 579 (1970).

(10) A. Hudson and K. D. J. Root, *Advan. Magn. Resonance*, **5**, 1 (1971).

(11) Apparently, the thermal decomposition of **1** in cyclohexanone^{12a} or hexachlorobutadiene^{12b} gives more information about these species.

(12) (a) L. S. Kobrina, L. V. Vlasova, and V. I. Mamatjuk, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **2**, 92 (1971); (b) J. Bargon, *J. Amer. Chem. Soc.*, **93**, 4630 (1971).

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Thermal Generation of Organic Molecules in Electronically Excited States. Evidence for a Spin Forbidden, Diabatic Pericyclic Reaction¹

Sir:

The understanding of the mechanisms by which molecules undergo reactions involving a change in electronic state is among the more intriguing problems occupying the attention of photochemists,² spectroscopists,³ and kineticists.⁴ Many types of interesting questions can be asked concerning interconversion of electronic states (*i.e.*, electronic relaxation³) during

(1) Molecular Photochemistry. LXII. Paper LXI: A. Yekta and N. J. Turro, *Chem. Phys. Lett.*, **17**, 31 (1972). Paper LX: R. R. Hautala and N. J. Turro, *Mol. Photochem.*, **4**, 536 (1972). The authors gratefully acknowledge the generous support of this work by the Air Force Office of Scientific Research (Grant No. AFOSR-70-1848) and the National Science Foundation (Grant No. NSF-GP-26602x).

(2) G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969).

(3) For a timely review of the problem of radiationless transitions see J. Jortner, S. A. Rice, and R. M. Hochstrasser, *ibid.*, **7**, 149 (1969).

(4) H. Eyring, G. Stewart, and R. B. Parlin, *Can. J. Chem.*, **36**, 72 (1958); E. K. Gill and K. J. Laidler, *ibid.*, **36**, 1570 (1958).

a reaction such as the following. (a) Can a singlet-triplet conversion occur during a concerted reaction (*i.e.*, violation of Wigner's⁵ "spin conservation rule")? (b) Are specific vibronic interactions required to promote interconversion of electronic states, and, if so, which nuclear motions are most effective? (c) What are the relationships, if any, between unimolecular adiabatic ground-state reactions and radiationless transitions such as internal conversion, intersystem crossing, and primary photochemical reactions? (d) What are the electronic requirements for thermal generation of an electronically excited organic molecule? We report here a study of the effect of solvent on the activation parameters for thermolysis of tetramethyl-1,2-dioxetane (**1**), and we show how our new data, when coupled to information available in the literature and to the concepts of molecular spectroscopy, can lead to the inference of a rather detailed picture of the mechanism of decomposition of **1** and some fresh insights relevant to questions a-d, and demonstration of a close connection between some radiationless electronic relaxation processes and certain photochemical primary processes.

Solutions of **1** (approximately 0.05 M) in various aerated solvents were heated in a thermostated sample holder of a Hitachi-Perkin-Elmer spectrophotofluorimeter and the decay of intensity of acetone fluorescence was measured and taken to be the rate of fragmentation of **1**. The measured rates were strictly first order in all cases and have been shown⁶ to equal the rates of decomposition of **1**. The activation parameters for thermolysis of **1** in several solvents were then determined in a standard manner⁷ and are reported in Table I.

We now consider two distinct types of mechanisms to explain our new data and other previously reported data on the thermolysis of 1,2-dioxetanes, *i.e.*, the high yield of acetone triplets formed when **1** is thermolyzed.⁸ The first mechanism involves a transition state which very closely resembles a biradical (**2**), which can then be stabilized to the point of achieving the status of a real intermediate (eq 1); the second mechanism involves a structurally unspecified transition state (**1**[‡]) which proceeds directly to the observed products without the occurrence of any intermediates, *i.e.*, products are formed from **1** in an elementary chemical step.

Mechanism 1 might be expected (a) to proceed in nonpolar solvents with the occurrence of a substantially positive value of ΔS^{\ddagger} , based on analogy to the decomposition of di-*tert*-butyl peroxide⁹ ($\Delta S^{\ddagger} \sim +10$ eu) and the biradical-like fragmentation of cyclobutanes⁹ ($\Delta S^{\ddagger} \sim +10$ eu); (b) to show little variation in rate with structural substitution since the O-O bond breaking is dominant in achieving the transition state; (c) to exhibit a substantial rate increase in polar solvents

(5) The quantitative nature of the effect of spin conservation on the rate of a chemical reaction has not, except for statistical factors, been considered, to the best of our knowledge.

(6) The rate of disappearance of **1** was found to be identical when measured by nmr spectroscopy or fluorimetry.

(7) We feel that a very conservative error limit of our values of ΔH^{\ddagger} is ± 2 kcal/mol. Thus, perhaps the value of ΔH^{\ddagger} for acetonitrile as solvent is not much different than that for cyclohexane as solvent. Refinement of the data is in progress.

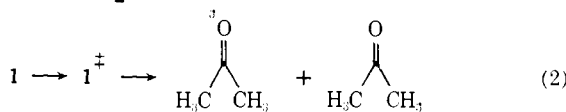
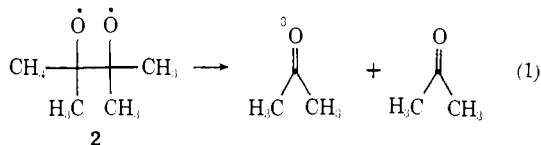
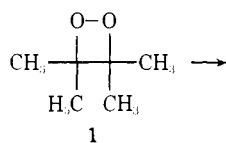
(8) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972).

(9) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21, 430, 269 (1960).

Table I. Thermolysis of 1,2-Dioxetanes

Molecule	Solvent	ΔH^\ddagger	ΔS^\ddagger	$k(\times 10^4)$ (55°), sec ⁻¹	Ref
	CCl ₄	22	-5	6	a
	CCl ₄	23	-4	3	b
	C ₆ H ₆ or c-C ₆ H ₁₂	25	-1	0.6	c
	CH ₃ CN	30	+11 ^d	0.4	c
	CH ₃ OH	13	-34 ^d	8.0	c

^a W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *J. Amer. Chem. Soc.*, **94**, 1619 (1972). ^b K. Kopecky and C. Mumford, quoted by H. E. O'Neal and W. H. Richardson, *ibid.*, **92**, 6553 (1970). ^c This work. See ref 7. ^d The values of ΔS^\ddagger could involve strong solvent effects and are therefore considered to be mechanistically ambiguous. The tremendous lowering of ΔH^\ddagger on dioxetane decomposition in protonic solvents is consistent with the previous work of Richardson: W. H. Richardson and V. F. Hodge, *Tetrahedron Lett.*, 2271 (1970); *J. Amer. Chem. Soc.*, **93**, 3996 (1971). For other examples of highly negative ΔS^\ddagger values for dioxetane decomposition, see W. Adam and H.-C. Steinmetzer, *Angew. Chem., Int. Ed. Engl.*, **11**, 540 (1972).



such as acetonitrile and methanol, in analogy to the work of Walling and Wagner¹⁰ on solvent effects on alkoxy radical decompositions; (d) to show a statistical production of three triplets per (excited) singlet. However, only criterion b is actually observed (Table I). The low values of ΔS^\ddagger are surprising and show little dependence on the number or type of groups attached to the ring carbon atoms. Although low values of ΔS^\ddagger can be rationalized by detailed thermochemical calculations,¹¹ the solvent effects seem to rule out the viability of mechanism 1, unless some further *ad hoc* assumptions are made. Furthermore, the biradical model provides no immediate understanding of the basis for the high yield of triplets⁸ observed when 1 is thermolyzed, *i.e.*, it does not explain straightforwardly the basis for the high yield of excited states (the diabatic

(10) C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, **86**, 3368 (1964).

(11) H. E. O'Neal and W. H. Richardson, *ibid.*, **92**, 6553 (1970).

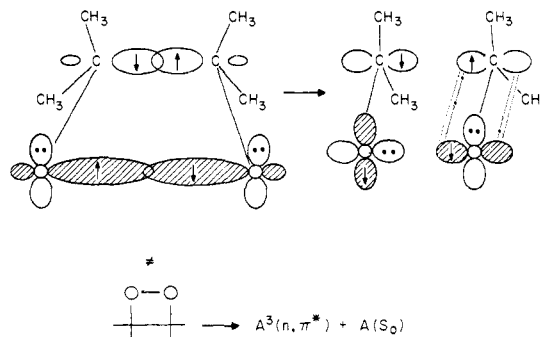


Figure 1. Mechanism for the thermolysis of 1. The homolytic cleavage of the σ_{OO} bond is imagined to involve preferred rotation about one of the CO axes (arbitrarily shown as the one on the left). This movement of electronic charge corresponds to an $n \rightarrow \sigma_{OO}^*$ excitation and (a) converts 1 smoothly into an n, π^* state and ground state and probably precedes a lagging C-C bond cleavage and (b) allows the orbital and spin decoupling of the incipient n and π^* electrons. For clarity, only two of the four n electrons on each oxygen are shown.

nature of the overall reaction) or the reason for the efficient singlet-triplet interconversion (eq 2).

We propose that a pericyclic mechanism can better handle the available data. We argue as follows. If the reaction is concerted, the rate determining transition state for fragmentation of 1 probably becomes asymmetric at some point, because only one of the acetone fragments can be efficiently electronically excited ($\Delta H^\circ + \Delta H^\ddagger \sim 125$ kcal; $E_3(\text{acetone}) \sim 78$ kcal/mol).¹² The asymmetry which leads to two different fragments is probably produced by an asymmetric vibration involving the O-O bond (coupled with the fragmenting C-C bond) which destroys the C_2 symmetry of the molecule.

Consider (Figure 1) the cleavage of the O-O bond of 1 as being nearly complete in the transition state 1^\ddagger and then consider the final products, an n, π^* state of acetone (A_*) and ground-state acetone (A_0). Notice that according to the elementary pictures of orbitals in the initial state (1^\ddagger) and final state ($A_* + A_0$), a 90° rotation of the bonding σ (p-like) lobe on the oxygen atom on the right, as the O-O bond breaks, converts this orbital into a p orbital on that oxygen. This electronic motion corresponds to an $n \rightarrow \sigma_{OO}^*$ electronic transition. If we consider the bond breaking as homolytic, this newly formed n orbital would be half-filled, *i.e.*, an n, π^* state is generated. Furthermore, the asymmetric vibronic motion which converts 1^\ddagger into A_* is formally analogous to that required for effective spin orbital coupling¹³ in an organic molecule, *i.e.*, the electron in the homolytically fragmenting bond is experiencing a strong "one-center" interaction with the oxygen nucleus and the electronic motion is that of a

(12) (a) A strain energy of approximately 26 kcal/mol for 1 is assumed. (b) For comments on the triplet energies of alkanones see J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).

(13) Spin-orbit coupling is commonly described in terms of angular momentum operators L_x , L_y , and L_z whose effect is to rotate any orbital upon which they operate through an angle of 90° about the x , y , and z axes. We interpret this idea in physical terms to mean that certain vibrations which represent a "torque" about an axis are most effective in inducing spin-orbital coupling. For a discussion of the spin-orbital coupling operator see S. P. McGlynn, T. Azumi, and M. Konoshita, "The Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 183. For factors enhancing spin inversion see L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

rotation about the C–O axis. Both of these factors should result in a substantial lowering of the normal prohibition to spin interconversion in a concerted reaction and thereby rationalize the astoundingly high yield of A_3 produced when **1** fragments! The diabatic nature (change from a ground to excited state surface) of the process is probably further facilitated by the similarity of 1^\ddagger to $(A_* + A_0)$ in energetics, electronic structure (Figure 1), and nuclear structure (r_{CO} of $A_* \sim 1.32 \text{ \AA}$, r_{CO} of $1 \sim 1.42 \text{ \AA}$).^{12b} In addition, the concerted model explains (a) the low, even negative values of ΔS^\ddagger for decomposition of **1** and other dioxetanes in nonpolar solvents as being due to the low probability that the proper vibrations¹⁴ needed to achieve 1^\ddagger will be found, even when the molecule has achieved sufficient activation energy;^{14b} (b) the lack of structural effects as being due to a leading O–O rupture in achieving 1^\ddagger ; and (c) the failure of a rate enhancement in acetonitrile as compensating ground- and transition-state stabilization, while methanol provides specific *transition state* stabilization, due to hydrogen bonding of the fragmenting O–O bond.

The driving force for favored triplet formation when **1** thermolyzes is probably the much lower energy of triplet **1** relative to singlet **1**, which causes a prior intersection of the ground-state energy surface of **1** and triplet energy surfaces leading to products. This conclusion finds strong corroboration in the theoretical analysis of 1,2-dioxetane decompositions reported by Kearns.¹⁵

To the best of our knowledge, this report represents one of the few attempts to apply the formalism of a spin-orbital coupling operator to assist in the understanding of a unimolecular chemical reaction of an organic molecule.¹⁶ We feel that the success of such a treatment should encourage further consideration of the use of the ideas on radiationless processes between electronic states long employed by molecular spectroscopists,³ to analyze certain chemical reactions, especially those involving generation of organic molecules in electronically excited states.

Acknowledgments. We are grateful to Drs. A. A. Lamola, W. H. Richardson, L. Salem, and K. Müller for very informative and stimulating discussions of the ideas presented in this paper.

(14) (a) Indeed, the activation parameters for decomposition of the three methylated 1,2-dioxetanes listed in Table I bear a striking resemblance to those for a classical pericyclic reaction, the ring opening of cyclobutenes to butadienes. For pertinent data see M. R. Willcott, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, **9**, 1 (1972). (b) The biradical mechanism can be maintained if one is willing to suppose that the solvent effects are ambiguous, the alkoxy model is a poor one, or that the triplet biradical has a much greater tendency to form products than the singlet biradical (which closes reversibly). Thus, the two mechanisms may be very similar in terms of predicting experimental response to various changes in structure and reaction conditions. However, we feel that some unusual observations, such as the tremendous stability of a bisadamantylidioxetane (J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972)), can be explained nicely on the basis of inhibition of the lowest energy vibronic motions for cleaving the O–O bond of the dioxetane.

(15) D. Kearns, *Chem. Rev.*, **71**, 395 (1971).

(16) For recent theoretical studies of radiationless processes see R. G. Gilbert and I. G. Ross, *Austr. J. Chem.*, **24**, 1541 (1971); T. Y. Chang and H. Basch, *Chem. Phys. Lett.*, **5**, 147 (1970).

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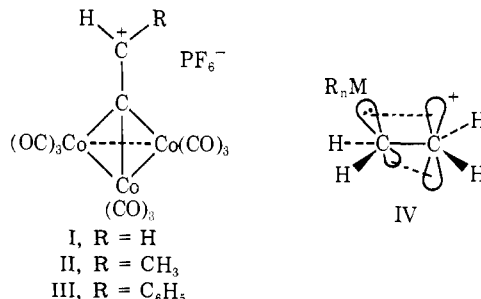
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Organocobalt Cluster Complexes. XI. Carbonium Ion Derivatives¹

Sir:

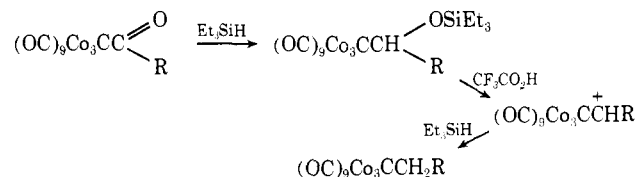
The stabilization of π -complexed carbonium ions in transition metal complexes is by now a well-known phenomenon,² but the stabilization of carbonium ions in σ -bonded organotransition metal structures is implied by only a few examples.³ We report here concerning three novel carbonium ion salts, I, II, and III,



whose stability we believe to be a direct consequence of their position relative to the three cobalt atoms in the cluster.

During the course of our studies dealing with carbon-functional alkylidynetricobalt nonacarbonyl complexes,^{1,4} we studied the reduction of acyl derivatives, $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{R}$.¹ Their direct reduction to the alkyls, $(\text{OC})_9\text{Co}_3\text{CCH}_2\text{R}$, by the action of triethylsilane and trifluoroacetic acid in THF solution proved to be a facile, high-yield process and this suggested to us that the cluster carbonium ions were readily accessible and possibly quite stable (Scheme I). The reaction course

Scheme I



shown implies that it is the presence of the trifluoroacetic acid which is responsible for the reduction to the alkyl derivative. If this is so, then reduction of acyl derivatives to the corresponding alcohols might be possible if the acid were omitted. Such was the case. Reaction of the $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{R}$ (R = H, CH₃, C₆H₅) with equimolar quantities of Et₃SiH in refluxing benzene under an atmosphere of carbon monoxide gave (after treatment of the mixture with concentrated H₂SO₄ and then with ice water) the expected alcohols: $(\text{OC})_9\text{Co}_3\text{CCH}(\text{OH})\text{R}$ (R = H, mp 161–163°, 46%; R = CH₃, mp 158–160°, 88%; R = Ph, mp 87–89°, 68%). These proved to be useful starting materials for the preparation of I, II, and III.⁵

(1) Part X: D. Seyferth and J. E. Hallgren, *J. Organometal. Chem.*, in press.

(2) M. L. H. Green in G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, 3rd ed, Methuen & Co., London, 1968.

(3) Reference 2, Chapter 7, especially pp 209–217.

(4) (a) D. Seyferth and A. T. Wehman, *J. Amer. Chem. Soc.*, **92**, 237 (1970); (b) J. E. Hallgren, C. S. Eschbach, and D. Seyferth, *ibid.*, **94**, 2547 (1972); (c) D. Seyferth and G. H. Williams, *J. Organometal. Chem.*, **38**, C11 (1972); (d) D. Seyferth, J. E. Hallgren, and P. L. K. Hung, *ibid.*, in press.

(5) Previous workers were unable to prepare such alcohols by direct reaction of $\text{Co}_2(\text{CO})_8$ with $\text{CX}_3\text{CRR}'\text{OH}$ (X = Cl, Br; R, R' = H, H; H, Me; Me, Me): G. Pályi, F. Piacenti, M. Bianchi, and E. Benedetti, *Acta Chim. Sci. Hung.*, **66**, 127 (1970).